

(NASA-CR-196810) PREBIOTIC POLYMER  
SYNTHESIS AND THE ORIGIN OF  
GLYCOLYTIC METABOLISM Report, 1  
Feb. 1993 - 1 Aug. 1994 (Search  
for Extraterrestrial Intelligence  
Inst.) 3 p

N95-70194

Unclass

Z9/27 0022355

PERFORMANCE REPORT  
(February 1, 1993 to August 1, 1994)

Grant Title: Prebiotic Polymer Synthesis and the Origin of Glycolytic Metabolism (NCC 2-784)

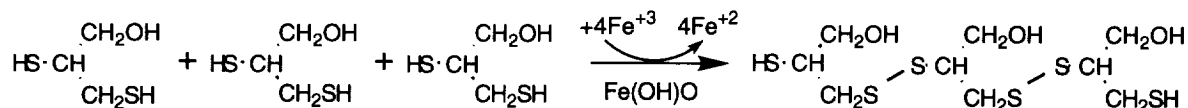
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**Summary:** In the past three years we have made significant progress in four research areas: 1) We developed a new model prebiotic polymer synthesis that yields polydisulfide polymers when dithiols are oxidized by iron(III) of synthetic minerals; 2) Our calculations of average oxidation number of the biocarbon of several types of organisms showed that the biosphere is very close to the reduction level of formaldehyde (oxid. number = 0); 3) Our estimates of the free energy of formation of biochemicals from one carbon substrates revealed that their energy of formation is determined mainly by the oxidation state of the one carbon precursor and the number of carbons in the product. These energy values can be used to predict the plausibility of prebiotic synthetic reactions; and 4) We calculated the free energy and the carbon redox disproportionation values for (a) 25 fermentation reactions, and (b) the biosynthesis of the *E. coli*'s amino acids, lipids, and nucleotides from glucose. We found that free energy of the fermentation reactions was directly proportional to the degree of redox disproportionation of carbon, and that the biosynthesis of amino acids and lipids was driven by the redox disproportionation of glucose that yielded a large amount of useful chemical energy. We concluded that the redox disproportionation of glucose carbon was the primary energy source of amino acid and lipid biosynthesis. These studies are discussed in more detail below.

#### Prebiotic Oxidative Polymer Synthesis

A major problem in the prebiotic synthesis of anhydride polymers like polypeptides and polynucleotides is the destruction of chemical condensing agents and reactive intermediates by water that prevents the formation of large polymers. As a way to overcome this problem we examined the prebiotic oxidative polymerization of the dithiol (2,3-dimercaptopropanol) by ferric ions on the surface of iron(III) hydroxide oxide (reaction shown below).



Polydisulfide polymers up to 15 units long were synthesized from low concentrations of dithiol monomer (1mM) under mild conditions (pH 4, 40°C, 3 days). Synthetic goethite ( $\alpha\text{-Fe(OH)O}$ ) and synthetic magnetite ( $\text{Fe}_3\text{O}_4$ ) gave similar yields of oligomers. The oxidative polymerization 2,3-dimercaptopropanol is an attractive prebiotic reaction because it needs only a small three carbon monomer, 2) occurs readily at low monomer concentration (1 mM) to give reasonably large oligomers (up to 15-mer) under mild conditions, and 3) water does not interfere chemically in the reaction. Ferric ions needed for the formation of  $\text{Fe(OH)O}$  and  $\text{Fe}_3\text{O}_4$  on the primitive Earth could have been continually generated by photooxidation of dissolved ferrous ions.

#### Estimation of the Reduction Level of Biocarbon

In order to better understand the chemical dynamics of metabolism we calculated the average oxidation number of the biocarbon of several types of organisms. The oxidation number of carbon ranges from +4 for carbon dioxide the most oxidized form of carbon to -4 for methane the most reduced form of carbon. The average oxidation number of biocarbon was calculated from the biochemical

composition of the organisms and the average oxidation number of the each biochemical components (protein, lipid, polysaccharide, and nucleic acid). We found that the reduction level of the biocarbon of most plants and microbes was between +0.04 and -0.22. Since over 99% of the carbon of the biosphere resides in microbes and land plants (90% in forests), our calculations established that the average oxidation number of the carbon of the Earth's biosphere was near 0.10 -- a value near the reduction level of formaldehyde (oxid. # = 0.0) which requires 4 electrons to be synthesized from carbon dioxide. We also found that for every type of organism, the average reduction level of the products of biosynthesis was very close to that of formaldehyde (oxid. # = 0.0), if the carbon dioxide by-product of lipid biosynthesis was included in the calculation.

### **Estimation of the free energy of formation of biochemicals**

We also calculated the standard free energy ( $\Delta G^\circ$ ) of formation of amino acids, nucleosides, sugars, and fatty acids from simple one carbon precursors. These energy values can be used to estimate the plausibility of prebiotic reactions, because they indicate the degree to which reactants or products are favored in a reaction at equilibrium under standard conditions. Values were calculated for the synthesis of each of the 20 protein amino acids and 12 amino acids from spark discharge experiments from one carbon precursors (carbon dioxide, formic acid, formaldehyde, methanol, or methane) and inorganic nitrogen ( $\text{NH}_3$  or  $\text{N}_2$ ). Water acted as a source of hydrogen or oxygen. Values were also calculated for carbon dioxide reactions using other reductants ( $\text{H}_2\text{S}$ ,  $\text{Fe}^{+3}$ , or  $\text{H}_2$ ). Energy values were also estimated for the synthesis of sugars, nucleotides, fatty acids from carbon dioxide, dinitrogen (ammonia), and water.

We found that the energetic favorability of amino acid synthesis using one carbon substrates decreased in the order: formaldehyde = methanol > methane > formate > carbon dioxide. This plot indicated that amino acid synthesis was most favorable when the reduction level (oxid. #) of the carbon substrate was close to that of the amino acid. These calculations also showed that the synthesis of amino acids became more unfavorable as the number of carbons in the amino acid product increased. In the spark discharge syntheses using methane, ammonia and water no amino acids having an energy of formation greater than 130 kcal/mol were synthesized in detectable yields. We believe that this energy limit of 130 kcal/mol can be used to predict that substances like adenosine requiring 350 kcal/mol would not be synthesized in detectable yields in similar spark discharge reactions.

### **Redox disproportionation in fermentation and biosynthesis**

In contemporary life one carbon compounds are converted to formaldehyde or its adducts (sugar groups and serine's hydroxymethyl group) before they enter biosynthetic metabolism. This observation that carbon enters biosynthesis at the reduction level of formaldehyde (oxid. # = 0.0), together with our earlier finding that the products of biosynthesis also have an average oxidation number near 0.0, indicates that biosynthesis is primarily a redox disproportionation process where electrons are exchanged between carbons without changing the average reduction level (oxid. #) of the processed carbon. This observation raises the question why does biosynthesis start with carbon at the formaldehyde level and then proceed by disproportionation. In order to answer this question, we calculated the Gibbs free energy change for 25 carbon fermentation reactions, and for amino acid, lipid, and nucleotide biosynthesis from glucose. We also calculated the degree of redox disproportionation of carbon of these processes. The redox disproportionation of a reaction was defined as the sum the absolute values of the change in the oxidation number of all carbons in a reaction.

From these studies we concluded that:

- 1). Carbon fermentation processes derive their energy from the redox disproportionation of carbon groups, and that the energy yield of these fermentation processes is directly proportional to the degree of redox disproportionation.
- 2). Amino acid and lipid biosynthesis are essentially fermentative processes that are driven by the very favorable energetics of the redox disproportionation of glucose carbon. Although amino acid and lipid biosynthesis yield as much the ATP as they consume, nucleotide biosynthesis which is not driven by redox disproportionation has to rely completely on exogenous sources of ATP -- anhydride energy.
- 3). The use of redox disproportionation of carbon to obtain energy in fermentation and biosynthesis is predetermined by the chemistry of carbon that establishes the direction of electron flow. The direction of electron transfer is from more oxidized hydrogen-containing carbon groups with larger negative reduction potentials to more reduced carbon groups to give a product that is a weaker reducing agent.

### Implications

The above studies suggest that biosynthetic transformations are primarily redox processes that are driven by the energy made available from the redox disproportionation of carbon groups at the at the sugar (formaldehyde) reduction level (oxidation number = 0.0) Since this biochemical dynamic is predetermine by the chemistry of carbon, other carbon-based life in the universe will probably have a similar sugar-based disproportionative metabolism that yields biocarbon at the reduction level of formaldehyde. Furthermore, other carbon-based intelligent life in the universe will be aware of this shared property and surmise our knowledge of it. Therefore, we proposed that this common knowledge could lead to the selection of a microwave frequency based on formaldehyde (like the 72.8 GHz line of the 0,0,0-->1,1,1 rotational transition of formaldehyde) as an interstellar contact channel.

### Publications:

- Weber, A.L.(1993) A biochemical magic frequency based on the reduction level of biological carbon. In: *Proceedings of the 1993 Bioastronomy symposium: Progress in the search for extraterrestrial life*, Santa Cruz, California, August 16-20, 1993, S. Shostak (ed.), Astronomical Society of the Pacific, in press.
- Weber, A.L. (1994) Prebiotic polymerization: oxidative polymerization of 2,3-dimercapto-1-propanol on the surface of iron (III) hydroxide oxide. *Origins of Life and Evolution of the Biosphere*, 24, in press.
- Weber, A.L.(1993) A redox beginning: which came first phosphoryl, acyl, or electron transfer. In: *Abstracts, 7th ISSOL Meeting and 10th International Conference on the Origin of Life*, Barcelona, Spain, July 4-9, 1993, p. 42.
- Weber, A.L.(1993) A biochemical magic frequency. In: *Abstracts, 1993 Bioastronomy Symposium: Progress in the search for extraterrestrial life*, Santa Cruz, California, August 16-20, 1993, p. 32.
- Weber, A. L. (1994) Prebiotic oxidative polymerization of 2,3-dimercaptopropanol on the surface of iron(III) hydroxide oxide. In: *Abstracts, 207th American Chemical Society National Meeting*, San Diego, Calif., March13-17,1994, Division of Geochemistry, abstract no. 43.
- Weber, A. L. (1994) Redox energy sources for the origin of metabolism and prebiotic polymerization. In: *Abstracts, Fifth Symposium on Chemical Evolution & the Origin and Evolution of Life*, NASA Ames Research Center, Moffett Field, Calif., April 25-29, 1994, abstracts alphabetically listed.